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A brand new zeolite catalyst for carbonylation reaction

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1. Catalyst preparation

The reagents used for EU-12 zeolite synthesis included aluminum hydroxide (Al(OH)$_3$ ·1.0 H$_2$O, Aldrich), rubidium hydroxide (RbOH, 50 wt% aqueous solution, Aldrich), colloidal silica (Ludox AS-30, 30 wt%, Aldrich) and Choline chloride (ChCl, 99 wt%, Wako), sodium hydroxide (NaOH, 99 wt% Wako). The final composition of the synthesis mixture was 2.0ChCl: 0.3Rb$_2$O: 0.7Na$_2$O: 0.25Al$_2$O$_3$: 5SiO$_2$: 100H$_2$O. In a typical run, Al (OH)$_3$ and RbOH were slowly added into distilled water with magnetic stirring to prepare an aluminate solution. Then a mixture of colloidal silica, ChCl and water was added into the prepared aluminate solution and was kept stirring for 24 h. Finally, the synthesis mixture was subjected to a hydrothermal treatment at 150 ^{o}C under 5 rpm rotation for 7 days. The resultant product was filtered, washed repeatedly with deionized water, and dried overnight at 100 ^{o}C. As-synthesized zeolite was calcined under air atmosphere at 600 °C for 6 h to remove the organic structure-direction agent (OSDA), as made EU-12. The calcined sample was then exchanged three times in 1.0 M ammonium nitrate (NH$_4$NO$_3$, 99 wt%, Wako) solution at 80 ^{o}C for 6 h followed by drying at 110 ^{o}C overnight and calcination at 550 ^{o}C for 4 h in order to obtain its proton (H$^+$) form, which denoted as HEU-12.

For comparison purpose, we performed DME carbonylation reaction on commercial HMOR (12-MR: 6.5×7.0, 8-MR: 2.6×5.7 Å; SiO$_2$/Al$_2$O$_3$=18) and HZSM-35 (10-MR: 4.2×5.4, 8-MR: 3.5×4.8 Å; SiO$_2$/Al$_2$O$_3$ =18) zeolite under the same conditions to HEU-12. In addition, H-Beta (12-MR: 6.6×6.7, 5.6×5.6 Å; SiO$_2$/Al$_2$O$_3$=18), HZMS-5 (10-MR: 5.1×5.5, 5.3×5.6 Å; SiO$_2$/Al$_2$O$_3$=24) and HY (12-MR: 7.4×7.4 Å SiO$_2$/Al$_2$O$_3$=15) were also chosen to study their DME carbonylation performance under the same reaction conditions to HEU-12. All of the samples were purchased from Tosoh Catalyst Plant (Tosoh CO., Tokyo, Japan).

The Cu/EU-12 (0.8 wt% Cu, measured by XRF) zeolite was prepared by ion-exchange method. First, 0.02 mol/L Cu (NO$_3$) solution was prepared, and EU-12 was added to this solution to form a suspension. After stirred at 80 ^{o}C for 8 h, it was filtered, washed with excess deionized water, and then dried at 100 ^{o}C overnight. The final sample was calcined at 500 ^{o}C for 5 h in air. Before reaction, the Cu/EU-12

sample was reduced at 300 $^\circ$C for 4 h in H_2 atmosphere

The produce of regeneration spent EU-12 zeolite was referred the method reported by Lucas et al..[1] The spent EU-12 zeolite after reaction for 50 h was calcined at 200 $^\circ$C for 1 h under air atmosphere, then heated to 500 $^\circ$C and maintained for 2 h, and finally heated to 700 $^\circ$C for 0.5 h.

2. Catalyst characterization

Powder X-ray diffraction (XRD) pattern of the HEU-12 zeolite was recorded on a Rigaku D/max-2550V diffractometer by employing $Cu_{k\alpha}$ radiation (λ=1.54056 Å) at room temperature. Data points were acquired by scanning at a rate of 0.02° s^{-1} from 2θ= 5° to 2θ= 50°. The surface morphology and average size of HEU-12 zeolite were observed using a scanning electron microscope (SEM, JEOL JSM-6360LV). NH_3 temperature-programmed desorption (NH_3-TPD) was performed by using a BELCAT-B-TT catalyst analyzer (BEL Japan CO. Ltd.) equipped with a thermal conductivity detector (TCD) to characterize the acidic property of zeolite. In a typical procedure, 40 mg of sample was pretreated in flowing helium gas (He, 30 mL min^{-1}) at 500 °C for 1 h and then cooled down to 100 $^\circ$C. At this temperature, the sample was purged with He for 30 min and then 5% NH_3 in Ar passed over the sample for 30 min. The treated sample was subsequently purged by He at the same temperature for 30 min to remove physically adsorbed NH_3. TPD was performed in flowing He (30 mL min^{-1}) from 100 to 800 °C with a heating rate of 10 °C min^{-1}. Thermogravimetric (TG) analysis of the fresh EU-12 sample without calcination was performed on a Shimadzu DTG-60 thermal analyzer. In a typical TG measurement, the temperature was heated from room temperature to 900 $^\circ$C with a ramping rate of 10 $^\circ$C min^{-1} under air atmosphere. Nitrogen absorption/desorption isotherms were measured at -196 $^\circ$C using Micromeritics 3Flex analyzer. Prior to measurement, the samples were degassed at 200 $^\circ$C under vacuum for 4 h. The total surface area was calculated using the Brunauer-Emmett-Teller (BET) method; the pore volume was obtained from the Horvath-Kawazoe (HK) equation; the micropore volume and external surface area were calculated by employing the t-plot method. The Si/Al molar ratio of HEU-12 zeolite was confirmed by energy dispersive X-ray fluorescence (XRF) spectrometry

(PHILIPS, PW2404R). The ^{27}Al and ^{29}Si Solid-state magic angel spinning (MAS) NMR spectra were carried out on JEOL JNM-ECX500 spectrometer.

3. Catalytic testing

The catalytic performance valuation of HEU-12 zeolite was conducted in a packed-bed stainless steel reactor (9.5 mm outside diameter) heated by an external heater. The prepared catalyst was sieved into 20-40 mesh. In a typical run, 0.5 g zeolite was loaded into the reactor. Prior to reaction, catalyst was heated to 500 ^{o}C and kept for 3 h to remove impurity and adsorbed water under N_2 flowing. Then, the feedstock gas consisting of 3.03% Ar/4.13% DME/92.84% CO with 1.5 MPa was introduced into reactor at 20 mL/min. The effluent gas was analyzed by an online gas chromatograph (GC) equipped with TCD (Porapak Q column for DME and Activated carbon column for Ar, CO, CO_2 and CH_4), while the methyl acetate (MA) and methanol (MeOH) in off-gas were collected by ice trap using 1-butanol as solvent. The liquid products were analyzed by another Shimadzu 2014-8A equipped with a flame-ionization detector (FID) with a Gaskuropack 54 column. Internal standard quantitation method was used to determine the amount of MA and MeOH with 1-propanol as internal standard. All of the products selectivity in this report was calculated with molecular base. DME conversions (C_{DME}) as well as products selectivity (S_{MA}, S_{MeOH}, S_{CH_4} and S_{CO_2}) were calculated by the following equations:

$$C_{DME} = (X_{DME, in} /X_{Ar, in} - X_{DME, out} /X_{Ar, out}) / (X_{DME, in} /X_{Ar, in}) \times 100\%$$

$$S_{MA} = [MA]/ ([MA] + [Methanol] + [CH_4] + [CO_2])$$

$$S_{MeOH} = [Methanol]/ ([MA] + [Methanol] + [CH_4] + [CO_2])$$

$$S_{CO_2} = [CO_2]/ ([MA] + [Methanol] + [CH_4] + [CO_2])$$

$$S_{CH_4} = [CH_4]/ ([MA] + [Methanol] + [CH_4] + [CO_2])$$

($X_{DME, in}$: mole fraction of DME in feed gas; $X_{DME, out}$: mole fraction of DME in exit gas; $X_{Ar, in}$: mole fraction of Ar in feed gas; $X_{Ar, out}$: mole fraction of Ar in exit gas; "[MA]", "[Methanol]" "[CH_4]" and "[CO_2]" stand for the amounts in products.)

4. Analysis of the spent HEU-12 zeolite

The coke-deposited sample was obtained after the DME carbonylation reaction at 220 ^{o}C for time on stream (TOS) of 50 h. The amount and location of the deposited

carbon in the spent HEU-12 were investigated by both quantitative and qualitative methods. For the quantitative analysis, the total coke weight was determined by TG analysis, assuming that the weight loss above 200 $^{\circ}$C of the spent HEU-12 zeolite was entirely due to coke combustion. The location of coke on the spent HEU-12 zeolite was determined by N_2 adsorption-desorption isotherm. The amount of internal coke in the zeolite micropores was calculated from the decrease in the micropore volume of the spent HEU-12 sample, as compared with the pristine HEU-12 sample. In this calculation method, we assumed that the coke density was 1.22 g $\cdot cm^{-3}$. The amount of external coke (coke deposited on the external surface) was calculated by subtracting the internal coke content from the total coke content and based on the assumption that the remaining micropores volume in the spent catalyst was fully accessible to N_2 molecules through the three dimensionally interconnected zeolite channels. The coke analysis method was reported by Ryoo at al.[2]

To reveal the nature of coke retained on spent zeolite, the soluble components of coke were determined by gas chromatographs-mass spectrometer (GC-MS) according to the method reported by Guisnet and Magnoux.[3] In this technique, 50 mg sample of spent zeolite was treated with 2 mL of HF acid (40%) in order to dissolve the zeolite and liberate the coke. 14 mL of dichloromethane (CH_2Cl_2) were added in order to recover the soluble coke compounds. Finally, the coke molecules soluble in CH_2Cl_2 was analyzed by GC-MS (Shimadzu, GCMS-TQ8050) equipped with a capillary HP-5MS column. Compounds were identified by comparing mass spectra with NIST 11 library data.

5. In situ DRIFT spectroscopy study

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was performed on a Nicolet Nexus 470 FTIR spectrometer equipped with a diffuse reflectance attachment and with a MCT detector. The catalyst powder weighing about 20 mg was placed in a diffuse reflectance infrared cell with a ZnSe window. The spectra were recorded by collecting 32 scans at 2 cm^{-1} resolution. Prior to adsorption, the HEU-12 sample was dehydrated under He atmosphere at 300 $^{\circ}$C for 2 h. In a typical experiment, the temperature was reduced to the reaction temperature after

pretreatment and the background spectrum was recorded prior to introduction of DME into the cell at ambient pressure. After the steady state was obtained, He was introduced to remove DME and the adsorbed groups. CO was then introduced for 30 min, followed by purging with He. Then the 3.03% Ar/4.13% DME/92.84% CO as reactant gas was introduced with the flow rate of 20 mL/min. Once the steady state was reached, He was flowed into the cell again.
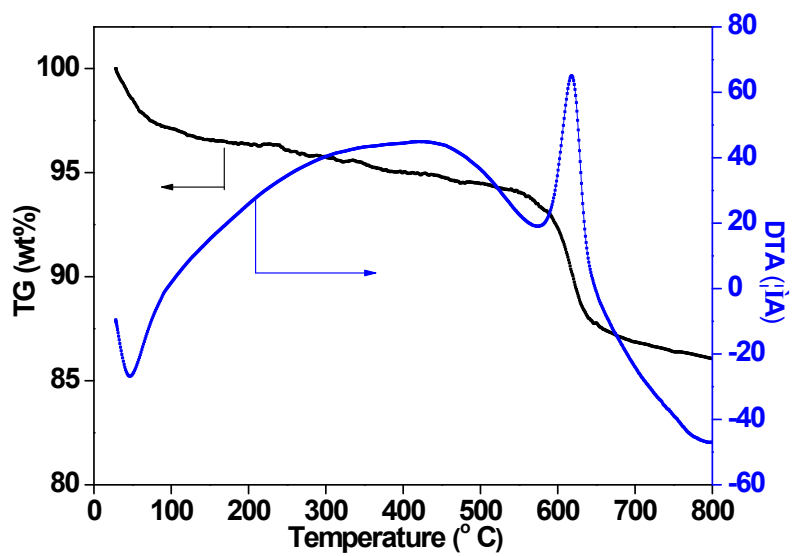
6. Supplementary Figures and Table

Fig. S1 TG/DTA curves of the fresh EU-12 sample without calcination.
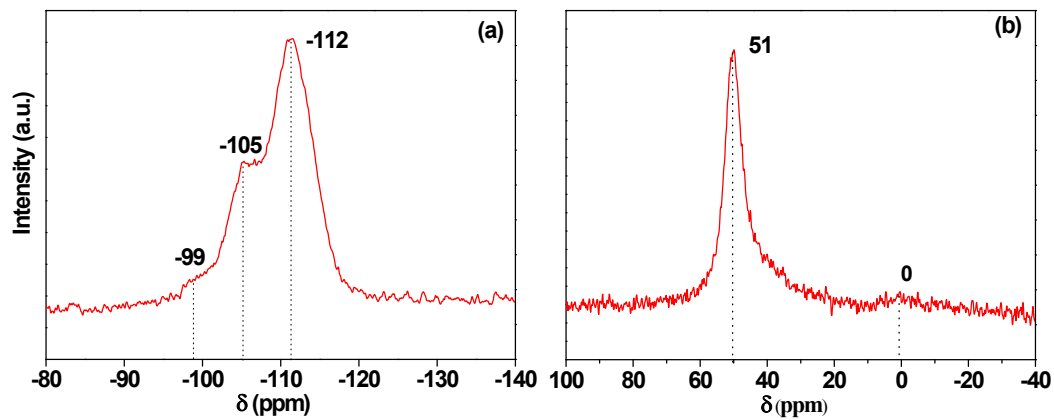
Fig. S2 (a) ^{29}Si MAS NMR and (b) ^{27}Al MAS NMR spectra of HEU-12 zeolite
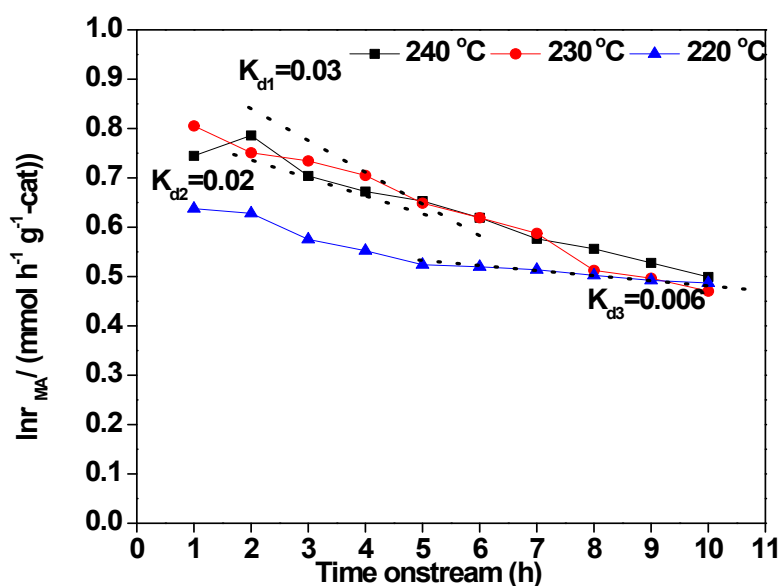
Fig. S3 Deactivation patterns on HEU-12 zeolite at 240 °C, 230 °C and 220 °C during DME carbonylation. Reaction condition: P=1.5 MPa, feed gas: 3.03% Ar/4.13% DME/92.84% CO, flow rate = 20 mL/min, weight $_{(zeolite)}$ = 0.5 g.

Fig. S3 compares the deactivation rete constants (k_d) of DME carbonylation on HEU-12 zeolite at 220-240 °C. The rate constants were designated as K_{d1}, K_{d2} and K_{d3} corresponding to the reaction temperature of 240, 230 and 220 °C, respectively. The K_d values were derived from the production rates of MA using the power-law equation. [4,5]

$-r_d = -d\alpha /d_t = k_d \alpha^a$

The r_d is the deactivation rate, α is the relative activity of the catalyst at time t (h), and a is the order of deactivation.[4] At 240 °C, the fast deactivation rate constant, k_{d1} was 0.03 h^{-1}, whereas k_{d3} was only 0.006 h^{-1} at 220 °C.
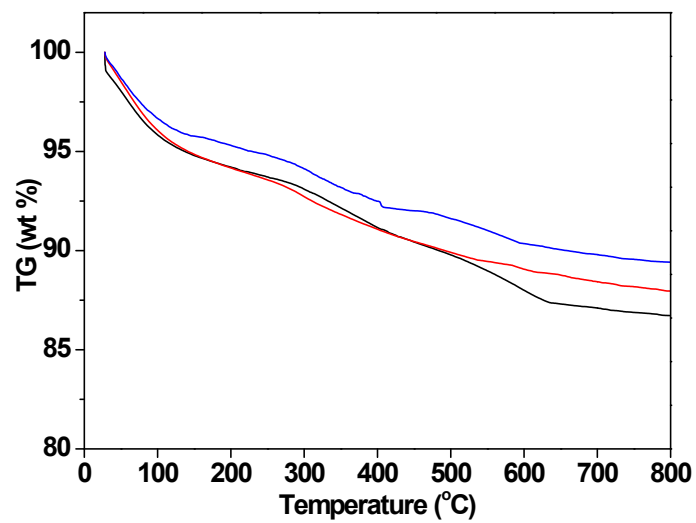
Fig. S4 The TG curves of the spent HEU-12 zeolite after reaction at 220 ^{o}C (blue line), 230 ^{o}C (red line) and 240 ^{o}C (black line).
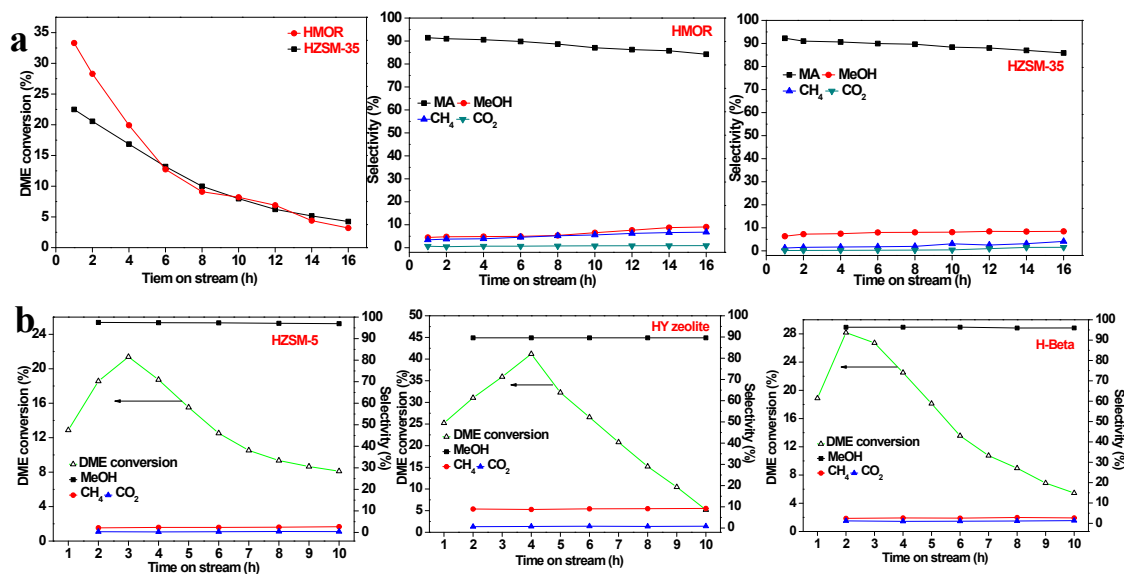
Fig. S5 (a) DME carbonylation performance over HMOR and H-ZSM-35 zeolite; (b) DME carbonylation performance over HZSM-5, HY, and H-Beta zeolite; reaction condition: T=220 °C, P=1.5 MPa, feed gas: 3.03% Ar/4.13% DME/92.84% CO, flow rate= 20 mL/min, Weight $_{(zeolite)}$=0.5 g, MeOH=methanol.
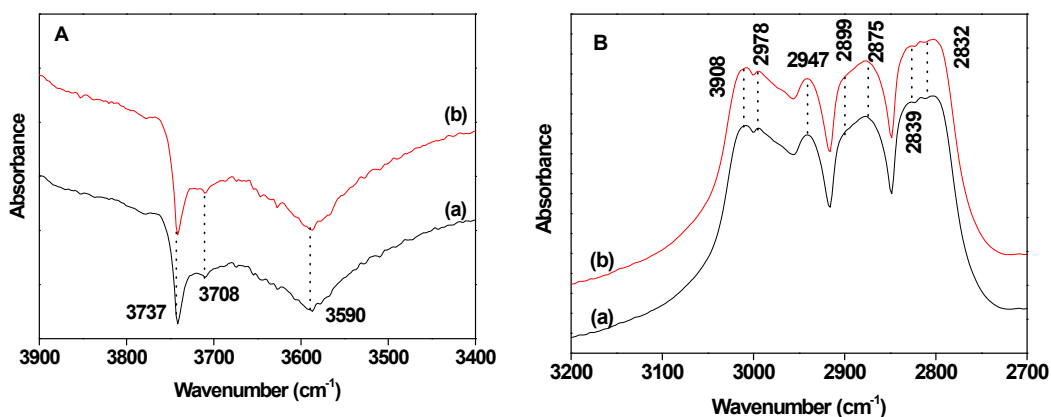
Fig. S6 In situ DRIFT spectra in O-H and C-H regions of DME adsorption over HEU-12 for (a) 5 min and (b) 10 min at 220 °C (A: O-H region, B: C-H region).

Three negative bands at 3737, 3708 and 3590 cm^{-1} were induced after exposure to DME gaseous. Generally, the band at 3590 cm^{-1} is attributed to DME interaction with the Bønsted acid sites in 8-MR channels. The bands at 3708 and 3737 cm^{-1} are associated with the AlOH and the internal and terminal or external SiOH groups, respectively.[7] A series of broad peaks are observed in the range of 2700-3100 cm^{-1}, which is attributed to the symmetric and asymmetric C-H stretching of methyl, indicating the generating of methoxyl species by DME reaction with the Brønsted acidic sites.[8]
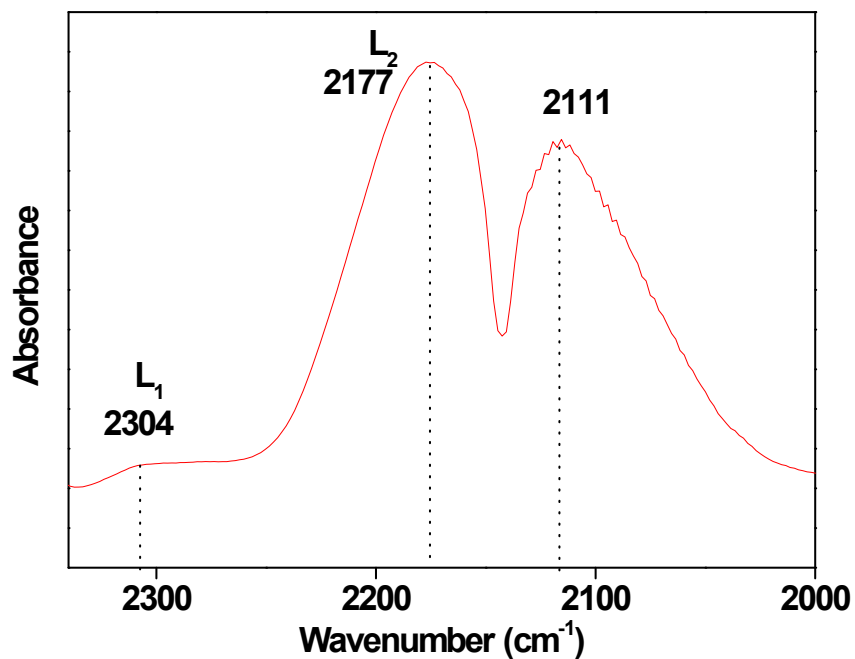
Fig. S7 In situ DRIFT spectrum over HEU-12 zeolite with adsorbed CO at 220 °C.

The weak L_1 (2304 cm^{-1}) band is attributed to CO on strong Lewis acid sites (e.g., extra-framework Al^{3+}) and L_2 (2177 cm^{-1}) sites correspond to penta-coordinated Al^{3+} site while the peak at 2111 cm^{-1} is assigned to CO interested with acidic O-H groups via H-bonding.[9]
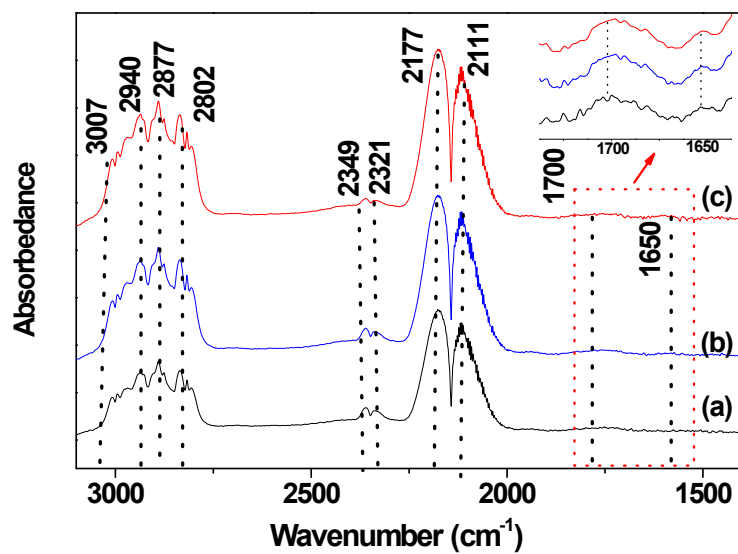
Fig. S8 In situ DRIFT spectra over HEU-12 zeolite after exposure to DME/CO/Ar for (a) 2 min, (b) 5 min and (c) 10 min at 230 °C.
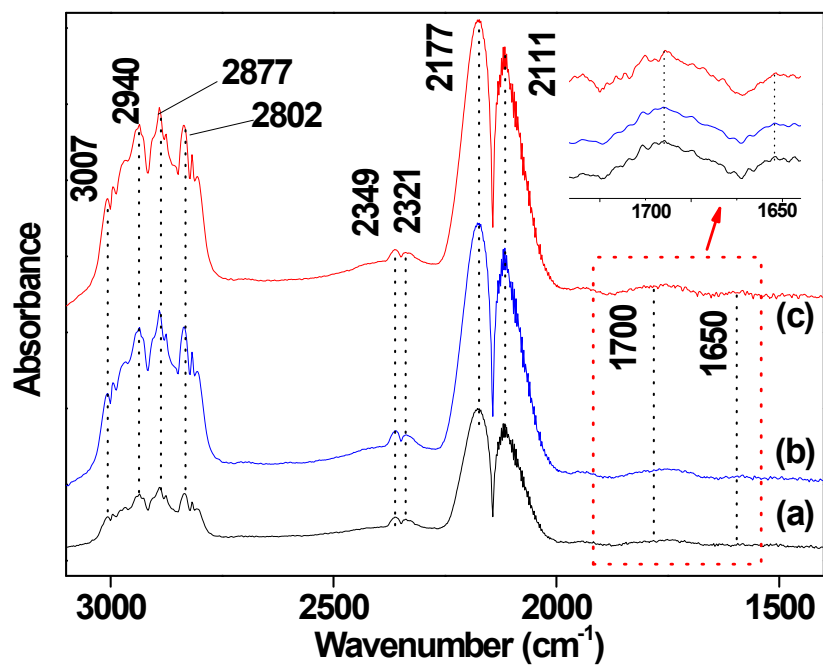
Fig. S9 In situ DRIFT spectra over HEU-12 zeolite after exposure to DME/CO/Ar for (a) 2 min, (b) 5 min and (c) 10 min at 240 °C.
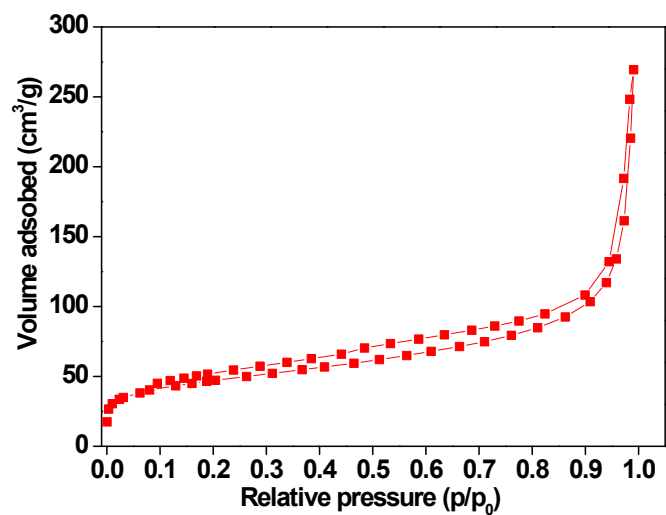
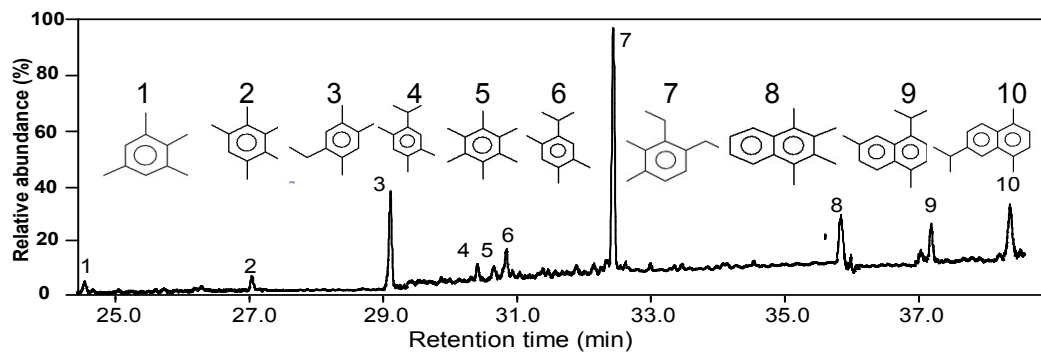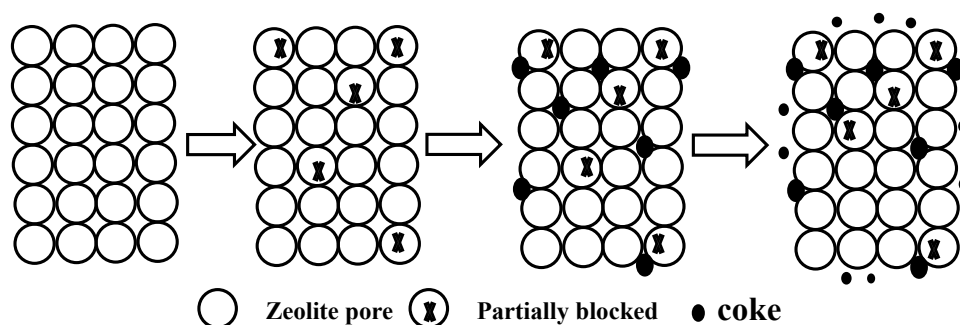Fig. S10 Nitrogen adsorption-desorption isotherms of the spent HEU-12 zeolite after reaction for 50 h at 220 ^{o}C.

Fig. S11 GC-MS analysis of the soluble coke in spent EU-12 zeolite.

○ Zeolite pore   (✕) Partially blocked   ● **coke**

Scheme S1 A possible model of coke formation on HEU-12 zeolite during DME carbonylation.

For the life time test of EU-12 zeolite, during the period of 0-10 h, the DME conversion decreased from 15.7% to about 12%, maybe due to the activation period of zeolite. Along with the reaction, a relative stable catalyst activity was observed in 10-20 h. During this reaction period, possibly only few coke precursors formed in part of channels and on the external surface of EU-12 zeolite, thus a stable DME conversion was achieved. The zeolite activity declines suddenly at the junction between two periods of 10-20 h and 30-50 h, and then become stable for a long time. Here, the coke formed in 20-30 h period maybe depresses the diffusion of reactants and products, therefore declining the catalyst activity suddenly.

At the period of 30-50 h, HEU-12 exhibited a stable DME conversion. During this stage, possibly few coke precursor deposite on the external surface of the EU-12 zeolite. This means that the coke has no effect on the diffusion rate of the reactants and products, thus resulting in a stable DME conversion. When the coke accumulated into a certain size to depress the diffusion of reactants and products, the zeolite activity decreased suddenly and entered into another stable phase.

It should be noted that no obvious change in the product selectivity was observed during the evaluation process. We believed that the deactivation was only attributed to the diffusion pathways partially blocked by the formed coke instead of the active acidic sites covered or poisoned by the coke. Therefore, the active acidic sites still possess the ability to convert DME into MA and keep stable product selectivity.
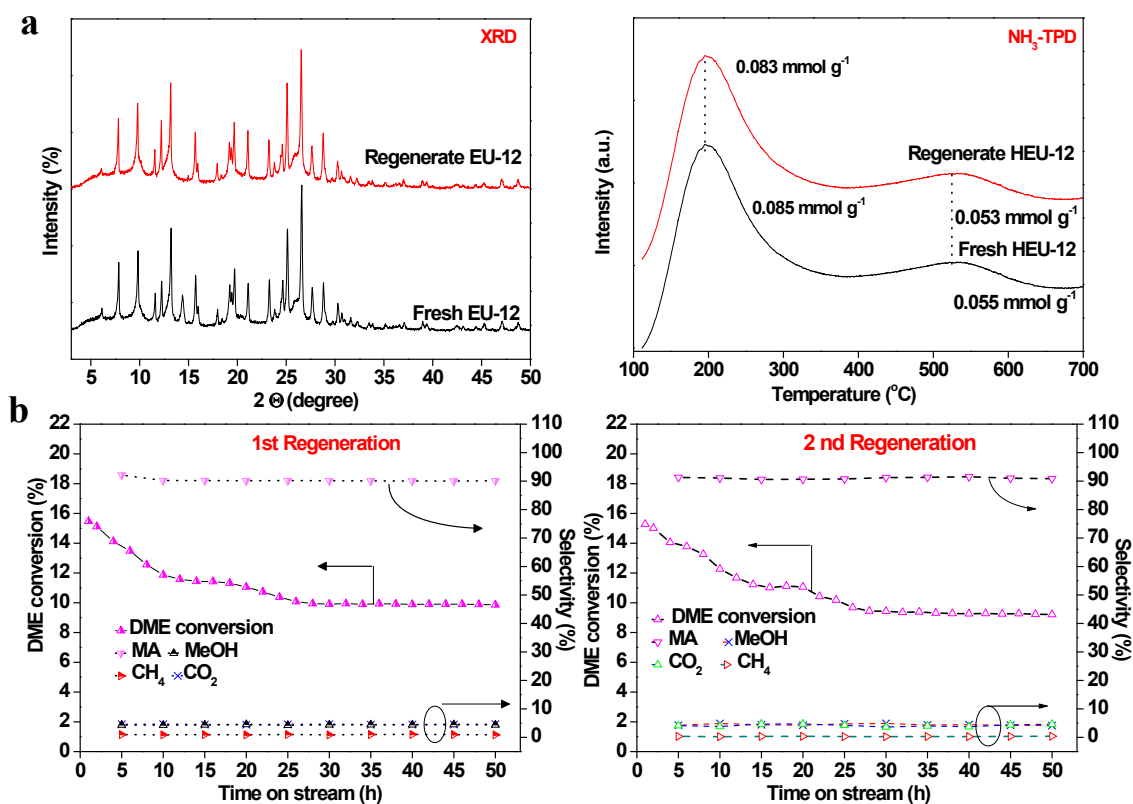
Fig. S12 (a) XRD patterns and NH$_3$-TPD curves of fresh and regenerated HEU-12 zeolite; (b) DME carbonylation performance over regenerated HEU-12; reaction conditions: T=200 ^{o}C, P =1.5 MPa, feed gas: 3.03% Ar/ 4.13 DME/ 92.84% CO; flow rate= 20 mL/min, weight $_{(zeolite)}$ =0.5 g.
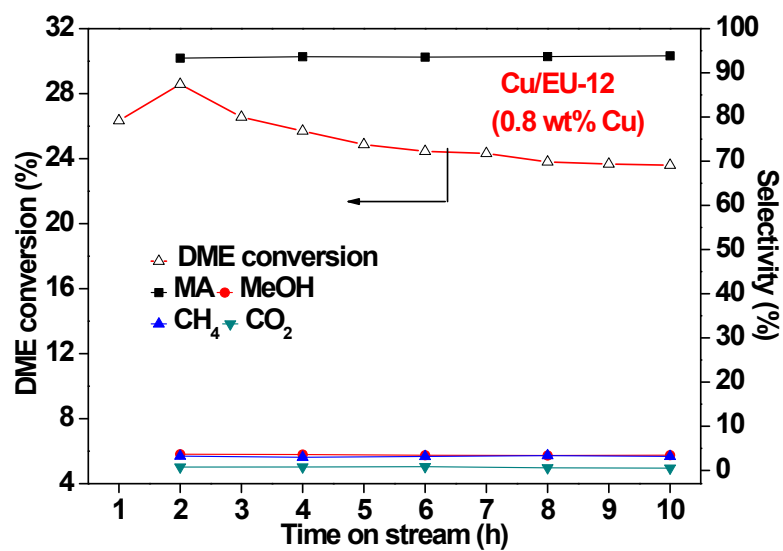
Fig. S13 The catalytic performance of DME carbonylation on Cu/EU-12 zeolite at 220 °C and 1.5 MPa. Reaction condition: feed gas: 3.03% Ar/ 4.13% DME/ 92.84% CO; flow rate = 20 mL/min, weight $_{(zeolite)}$ =0.5 g.

Table S1 Structural features and textural properties of HEU-12 and spent HEU-12 zeolite.

Sample	Si/Al	S_{BET} (m²/g)	S_{ext} (m²/g)	V_{total} (cm³/g)	V_{micro} (cm³/g)	Weak acidic sites [a] (mmol g⁻¹)	Strong acidic sites [a] (mmol g⁻¹)	Channel type [b]	Channel size [b] (Å)
HEU-12	8.3	330.2	80.9	0.588	0.494	0.085	0.055	3-D: 8-MR with side pockets	2.7×5.0 3.3×4.8 2.8×4.6
Spent HEU-12	—	309.5	64.4	0.574	0.472	—	—	—	—

[a] Estimation by NH_3-TPD curve: weak and strong acidic sites are in the range of 100-400 °C and 400-650 °C, respectively.

[b] Structural data obtained from the International Zeolite Association, see: http://www.iza-structure.org/databases/.

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